

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/US04/026926

International filing date: 18 August 2004 (18.08.2004)

Document type: Certified copy of priority document

Document details: Country/Office: US
Number: 60/538,105
Filing date: 20 January 2004 (20.01.2004)

Date of receipt at the International Bureau: 04 October 2004 (04.10.2004)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse

1231607

THE UNITED STATES OF AMERICA

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office

September 29, 2004

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM
THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK
OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT
APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A
FILING DATE.

APPLICATION NUMBER: 60/538,105
FILING DATE: *January 20, 2004*
RELATED PCT APPLICATION NUMBER: PCT/US04/26926

Certified by



Jon W Dudas

Acting Under Secretary of Commerce
for Intellectual Property
and Acting Director of the U.S.
Patent and Trademark Office



18351
U.S. PTO
012004

Practitioner's Docket No. 100325.0244PRO

PATENT

13441 U.S. PTO
60/538105
012004

Preliminary Classification
Proposed Class:
Subclass:

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: John Mak, Richard Nielsen, Thomas King Chow, Oliver Morgan, and Vincent Wai Wong

For: Methods and Configurations for Acid Gas Enrichment

Mail Stop Provisional Patent Application
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

COVER SHEET FOR FILING PROVISIONAL APPLICATION
(37 C.F.R. § 1.51(c)(1))

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 C.F.R. § 1.51(c)(1)(i). The following comprises the information required by 37 C.F.R. § 1.51(c)(1):

1. The following comprises the information required by 37 C.F.R. § 1.51(c)(1):

EXPRESS MAILING UNDER 37 C.F.R. § 1.10*

(Express Mail label number is **mandatory**).
(Express Mail certification is **optional**)

I hereby certify that this paper, along with any document referred to, is being deposited with the United States Postal Service on this date January 20, 2004 in an envelope addressed to the Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450 as "Express Mail Post Office to Addressee" Mailing Label No. EV389268227US.

Date: 1/20/04

Sara L Geer
Type or print name of person mailing paper


Signature of person certifying

WARNING: Certificate of mailing (first class) or facsimile transmission procedures of 37 C.F.R. 1.8 cannot be used to obtain a date of mailing or transmission for this correspondence.

*WARNING: Each paper or fee filed by "Express Mail" must have the number of the "Express Mail" mailing label placed thereon prior to mailing. 37 C.F.R. 1.10(b).

"Since the filing of correspondence under § 1.10 without the Express Mail mailing label thereon is an oversight that can be avoided by the exercise of reasonable care, requests for waiver of this requirement will not be granted on petition." Notice of Oct. 24, 1996, 60 Fed. Reg. 56,439, at 56,442.

2. The names of the inventors are (37 C.F.R. § 1.51(c)(1)(ii)):

1. John Mak
2. Richard Nielsen
3. Thomas King Chow
4. Oliver Morgan
5. Vincent Wai Wong

3. The title of the invention is (37 C.F.R. § 1.51(c)(1)(iv)):

Methods and Configurations for Acid Gas Enrichment

4. The name, registration, customer and telephone numbers of the practitioner are (37 C.F.R. § 1.51(c)(1)(v)):

Name of practitioner: Martin Fessenmaier
Reg. No. 46697
Tel. 714-641-5100
Customer No. 34284

5. The docket number used to identify this application is (37 C.F.R. § 1.51(c)(1)(vi)):

Docket No. 100325.0244PRO

6. The correspondence address for this application is (37 C.F.R. § 1.51(c)(1)(vii)):

Rutan & Tucker, LLP
611 Anton Blvd., Suite 1400
Costa Mesa, CA 92626
USA

7. Statement as to whether invention was made by an agency of the U.S. Government or under contract with an agency of the U.S. Government. (37 C.F.R. § 1.51(c)(1)(viii)).

This invention was NOT made by an agency of the United States Government, or under contract with an agency of the United States Government.

8. Identification of documents accompanying this cover sheet:

A. Documents required by 37 C.F.R. § 1.51(c)(2)-(3):

Specification:	No. of pages	7
Drawings:	No. of sheets	2

9. Fee

The filing fee for this provisional application, as set in 37 C.F.R. § 1.16(k), is \$160.00 for other than a small entity.

10. Fee payment

Fee payment in the amount of \$160.00 is being made at this time.

11. Method of fee payment

Charge Account No. 502191, in the amount of \$160.00.

A duplicate of this Cover Sheet is attached.

Please charge Account No. 502191 for any fee deficiency.

Date:

01/20/2004



Martin Fessenmaier
Registration No. 46697
Rutan & Tucker, LLP
611 Anton Blvd., Suite 1400
Costa Mesa, CA 92626
USA
714-641-5100
Customer No. 34284

METHODS AND CONFIGURATIONS FOR ACID GAS ENRICHMENT

Field of The Invention

The field of the invention is gas processing and sulfur removal.

5 Background of The Invention

There are numerous sources of natural or synthesis gas known in the art, and almost all of them contain H₂S in various quantities that require at least partial desulfurization prior to further processing or release into the atmosphere. For example, natural gas, refinery gas, synthesis gas (e.g., from gasification of residual oil or coke), or Fischer-Tropsch gas-to-liquids process (GTL) 10 gases often contain H₂S in significant amounts that would interfere with downstream processes. Furthermore, the sulfur content in the tail gas from the Claus reactors typically requires treatment before releasing the tail gas to the environment.

If H₂S is present in large quantities, removal is commonly accomplished by absorption in an alkaline solvent, usually with an amine solvent. H₂S is later regenerated or desorbed in a 15 regenerator in a stripper operating at a lower pressure and elevated temperature. The acid gas from the regenerator is then typically processed in a Claus plant where the H₂S is converted to elemental sulfur by sub-stoichiometric reaction with air or oxygen.

However, nearly all gas streams which contain H₂S also contain significant quantity of CO₂ and when such gases are simply scrubbed with an alkaline solution, CO₂ is co-absorbed 20 with the H₂S. This is particularly problematic where the ratio of CO₂ to H₂S in the gas stream is relatively high, as complete removal of both gases will often produce an acid gas weak in H₂S, which tends to cause various problems in the Claus plant. Among other things, the dilution effect of CO₂ in such acid gases lowers the net heating value in the acid gas and also reduces the 25 residence time in the Claus furnace, rendering sulfur conversion difficult. Moreover, such acid gases also contain significant quantities of contaminants (e.g., benzene, toluene, xylene) that generally must be destroyed in the Claus furnace, which is necessary for protection of the Claus reactor catalysts. Unfortunately, the CO₂ dilution effect in such acid gases tends to lower the furnace flame temperature, thereby making destruction of these contaminants difficult.

In extreme cases, where the H₂S content in the acid gas falls below 10%, a normal Claus reaction becomes impossible and additional processing steps must be employed to enhance the conversion process. Additionally, the dilution effect of CO₂ will increase the size of the Claus plant as the plant size is predominantly controlled by the total volumetric flow of acid gas.

5 Where the acid gas is unsuitable as feed to a Claus plant, preprocessing using a selective acid gas removal process is frequently necessary. In a typical preprocessing operation, two gas streams are produced via selective absorption of H₂S from the acid gas and subsequent stripping of the rich solvent. Thus, one gas stream predominantly comprises CO₂ that can be sent to a thermal oxidizer or incinerator for conversion of residual H₂S to SO₂, prior to being discharged
10 to the atmosphere via a stack. The other gas stream is typically enriched in H₂S and is then processed in a simple Claus plant.

15 Generation of a sweet CO₂ stream can be particularly advantageous. Unlike the tail gas stream from a Claus plant, a sweet CO₂ stream is essentially free of nitrogen and can be further compressed and utilized for enhanced oil recovery, or as a diluent for controlling the flame temperature (NO_x control) in a gas turbine of an IGCC. Another advantage of selective gas treating is in the processing of Claus plant tail gas to meet environmental requirements. A typical
20 Claus plant can recover about 95% of the sulfur contents in an acid gas stream. The residual sulfur content can later be removed and recovered in a tail gas unit, with the regenerated H₂S (via regeneration of the rich solvent) recycled back to Claus unit.

25 Known processes for selective H₂S removal from high CO₂ gases include the Stretford process, LOCAT and Sulferox unit. These processes employ complex catalyst-based chemistry to oxidize H₂S directly to sulfur. However, these units are often complex, difficult to operate, and are limited to relatively small capacity. Alternatively, various known amine based solvents capable of selectively removing H₂S can be used. For example, selective absorption processes can be based on blended tertiary amines (e.g., those comprising diisopropanolamine (DIPA), formulated methyldiethanolamine (MDEA), and other amine-organic solvent blends). Such solvents, particularly when combined with specially adapted absorber internal designs will minimize co-absorption of CO₂ (typically, such processes can concentrate the H₂S content by a

factor of three to five fold). Other processes for selective H₂S removal include the use of sterically hindered tertiary amino compounds described in U.S. Pat. Nos. 4,405,580.

In still further attempts to increase selectivity of absorption, special tray configurations can be employed to reduce the contact time with CO₂ to achieve the required selectivity. For 5 example, U.S. Pat. Nos. 4,278,621 and 4,297,329 and 4,678,648 describe special tray and packing designs in minimizing CO₂ contact time. Unfortunately, the use of such processes and/or devices provide in most cases only marginal benefit for treating a diluted acid gas stream.

Alternatively, as described in U.S. Pat. Nos. 4,198,386 and 4,093,701, selectivity is achieved by varying gas flow-rates using a plurality of absorption columns, and splitting the 10 absorber column into a number of absorption zones with controlled flow-rates of lean amine solvent. However, such systems typically require additional pipes and valves, and are often costly and complicated to operate. In yet further attempts to increase selectivity, H₂S absorption may be enhanced via temperature control. Generally, a reduction in absorption temperature slows the CO₂ absorption rate. However, the cost of operating a refrigeration unit render such an option 15 often uneconomical.

Therefore, and especially where a diluted acid gas feed is employed, currently known methods and configurations are often neither suitable nor economical. Thus, there is still a need to provide improved configurations and methods for selective acid gas enrichment.

Detailed Description

20 The inventors generally contemplate configurations and methods of selective H₂S absorption from various gases comprising H₂S and CO₂, and particularly from gases in which H₂S is relatively diluted. In one preferred aspect, contemplated configurations employ an amine solvent (*e.g.*, methyldiethanolamine based solvent for preferential H₂S absorption). Here, the dilute acid gas is first contacted with a lean solvent for selective removal of H₂S, thereby 25 producing (1) an overhead CO₂ vapor with ppm level of H₂S suitable for disposal in an incinerator, and (2) a H₂S rich solvent that is processed in a regenerator. The regenerator produces a H₂S enriched acid gas, a portion of which is contacted by a second amine contactor, producing an overhead CO₂ vapor with ppm level of H₂S suitable for disposal in an incinerator,

and a H₂S rich solvent that is recycled to the regenerator. The remaining portion of the H₂S enriched acid gas is sent to a Claus unit.

Consequently, in one aspect of the inventive subject matter, the inventors contemplate a configuration in which acid gas is selectively removed as exemplarily depicted in **Figure 1**. Here, 5 the feed gas is a diluted H₂S acid gas stream from a gas treating unit having a gas composition of 6% H₂S, 92% CO₂ and 1.0% C₁, 0.7% C₂ plus hydrocarbons and 3000 ppm BTEX (Benzene, Toulene and Xylene).

The feed gas stream 1 enters the unit at 120°F and 10 psig and is scrubbed in the first amine absorber 51 with a lean amine stream 2. In order to meet the emission requirement, the 10 H₂S content in the overhead stream 3 must be removed to meet 150 ppmv using about 1800 GPM lean amine. The lean solvent typically consists of 40% to 50% MDEA, although other solvents such as DIPA, hindered amine or other formulated tertiary amines can be used. The amine absorber 51 typically includes of 12 to 18 trays as needed to achieve the required H₂S removal efficiency. Typically about 85% to 90% of the feed gas CO₂ is rejected to the overhead 15 vapor in stream 3. The rich solvent stream 4 exits the bottom of the first absorber typically at 150°F to 170°F.

The rich solvent stream 4 is combined with the rich solvent stream 5 from the second absorber 52 forming stream 6, and the mixture is pumped by the rich solvent pump 54 forming stream 7. Stream 7 is heated with a lean/rich exchanger 55 using the heat content of the lean 20 solvent from the regenerator 53. The rich solvent is heated to about 210°F forming stream 8 and enters the top of regenerator 53.

Regenerator 53 uses 20 stripping trays and a wash section for desorbing the acid gas. Alternatively, other contacting device such as packing can be used. The acid gas in the rich solvent is stripped with heat applied at the bottom reboiler 57, producing an overhead stream 9 25 and a lean solvent stream 10. The lean solvent typically at 260°F is pumped by lean solvent pump 56 to about 50 psig forming stream 19, and the heat content of which is recovered in the lean/rich exchanger. The lean solvent stream 20 is further cooled with a cooler 58 to typically 100 - 110°F, forming stream 21. Ambient air, cooling water or chilled water system can be used for cooling.

It is generally preferred that the cooler outlet temperature should be kept as low as possible (most preferably 60°F to 80°F) since the lower temperature favors the equilibrium of H₂S absorption while slowing down the CO₂ absorption process, thereby improving the H₂S selectivity of the process. Stream 21 is split into two portions, stream 22 and stream 2 at a flow rate of 600 GPM and 1800 GPM respectively. Stream 22 is fed to the second absorber 52 while stream 2 is fed to absorber 51.

The overhead vapor 9 is cooled in the overhead air-cooler 59 forming stream 13 which is separated in the reflux drum 60 forming a liquid stream 15 and a vapor stream 14. Stream 14, predominantly comprising water, is pumped by reflux pump 61 forming stream 16 as reflux to the regenerator. The enriched acid gas stream 14 is split into two portions, stream 17 and stream 18. Stream 17 is routed to a second absorber 52 for further enrichment and stream 18 is sent to the Claus unit.

The volume of stream 17 is about 25% to 75% of stream 14, depending on the H₂S concentration in the feed gas. For a low H₂S content feed gas, a higher flow ratio in the range of 15 75% (and even higher) is necessary. This ratio can be reduced to about 25% (and even less) when the H₂S concentration is higher. In most feed gas compositions, enrichment to about 75% H₂S can be achieved. In addition, over 90% of the hydrocarbons and BTX components are rejected by this process to the CO₂ vent streams. The H₂S enrichment and the absence of BTEX in the enriched acid gas are greatly beneficial to the Claus unit.

20 Alternatively, the rich solvent from the amine absorber 51 is split into two portions as depicted in exemplary configuration of **Figure 2**. Here, stream 7 from the rich solvent pump 7 is split into stream 25 and stream 26. Stream 25 at a flow rate of 300 GPM to 400 GPM is cooled in cooler 62 to about 100°F and then routed to the lower section of the second absorber 52. This configuration re-uses the semi-loaded rich solvent from the first absorber for further absorption 25 in the second absorber. Consequently, it should be recognized that such configurations will reduce the overall solvent circulation, the regeneration size, and energy consumption. **Table 1** and **Table 2** summarize exemplary calculations for process performance for two different feed gas compositions (Table 1: 7% H₂S, Table 2: 16% H₂S).

Table 1

MOL. FRAC.	FEED GAS	CO2	ENRICHED ACID GAS
H2S	0.070	0.000	0.751
CO2	0.910	0.978	0.249
C1	0.010	0.011	trace
C2-C5	0.007	0.008	trace
BTEX	0.003	0.003	trace
MMscfd	50.00	45.34	4.66

Table 2

MOL. FRAC.	FEED GAS	CO2	ENRICHED ACID GAS
H2S	0.160	0.000	0.750
CO2	0.820	0.974	0.250
C1	0.010	0.013	trace
C2-C5	0.007	0.009	trace
BTEX	0.003	0.0034	trace
MMscfd	50.00	39.34	10.66

Thus, specific embodiments and applications of acid gas enrichment have been disclosed. It should be apparent, however, to those skilled in the art that many more modifications besides those already described are possible without departing from the inventive concepts herein. The inventive subject matter, therefore, is not to be restricted except in the spirit of the present

disclosure. Moreover, in interpreting the specification, all terms should be interpreted in the broadest possible manner consistent with the context. In particular, the terms "comprises" and "comprising" should be interpreted as referring to elements, components, or steps in a non-exclusive manner, indicating that the referenced elements, components, or steps may be present,
5 or utilized, or combined with other elements, components, or steps that are not expressly referenced.

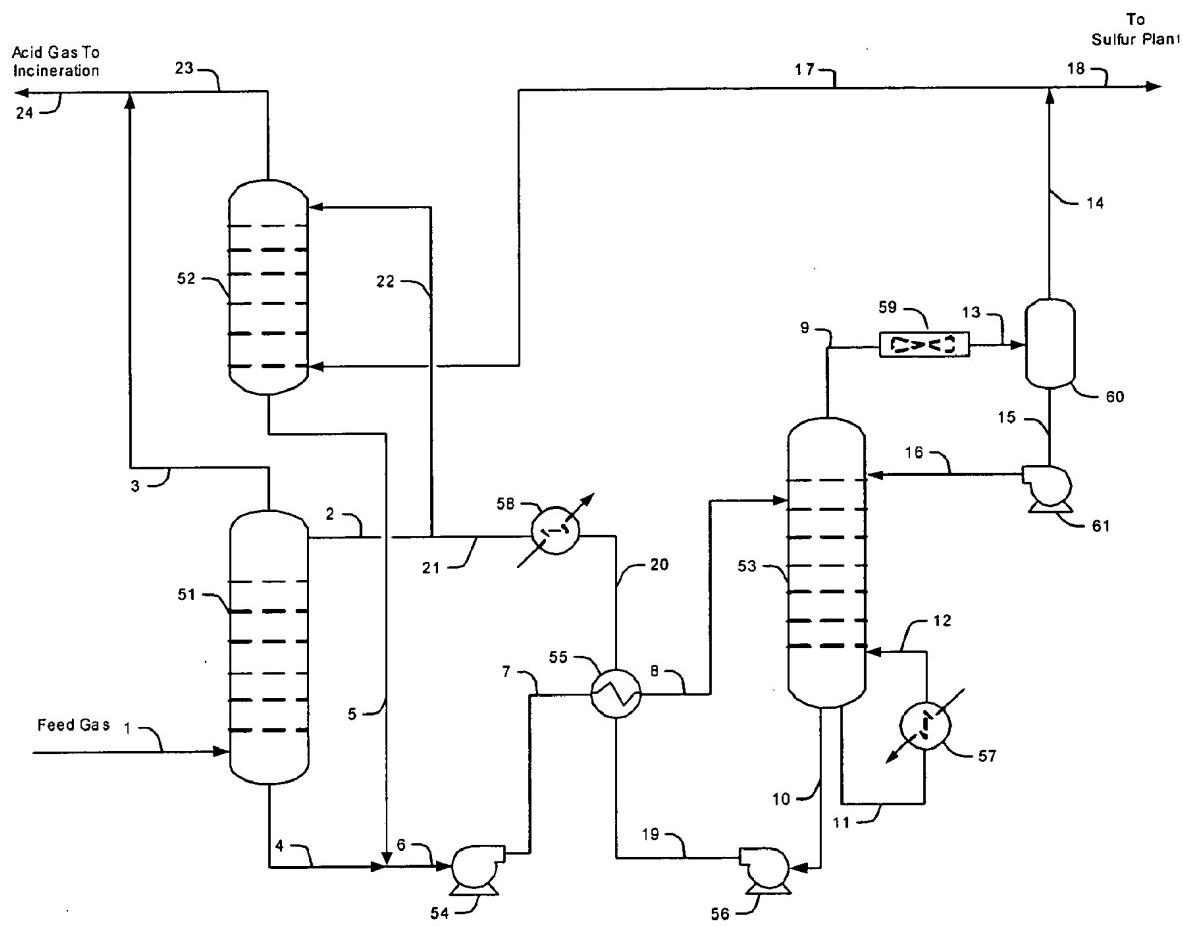


Figure 1

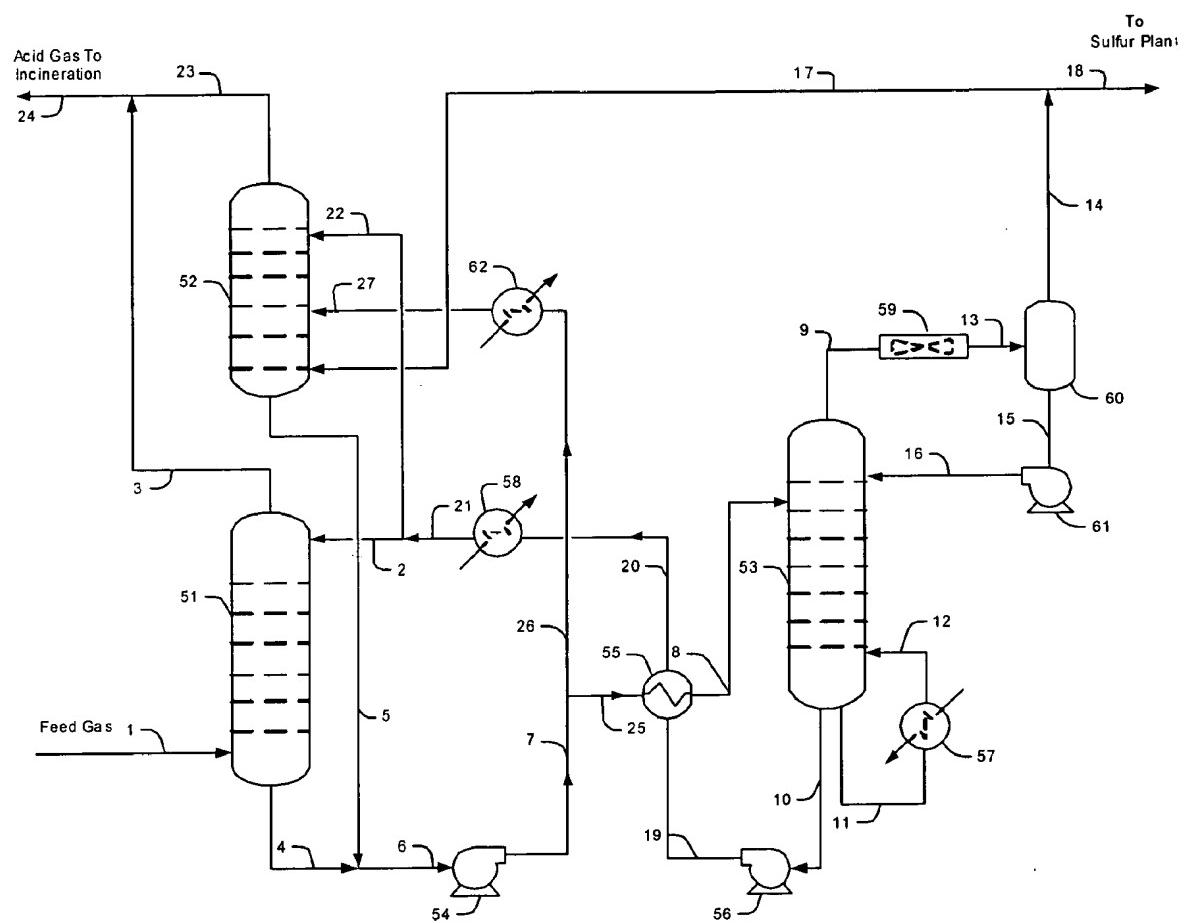


Figure 2